2005

Chemical openness and potential for misinterpretation of the solute environment of coastal sabkhat

Warren W. Wood
Michigan State University

Ward E. Sanford
U.S. Geological Survey

Shaun K. Frape
University of Waterloo, Waterloo, Ontario, Canada

ELSEVIER

Chemical Geology 215 (2005) 361–372

CHEMICAL GEOLOGY
INCLUDING
ISOTOPE GEOSCIENCE

www.elsevier.com/locate/chemgeo

Chemical openness and potential for misinterpretation of the solute environment of coastal sabkhat

Warren W. Wood[a,*], Ward E. Sanford[b], Shaun K. Frape[c]

[a]*Room 206 Nat. Sciences Building, Michigan State University, E. Lansing, Michigan 48824, USA*
[b]*MS 431 National Center, U.S. Geological Survey, Reston, Virginia 20192, USA*
[c]*Department of Earth Sciences, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1*

Accepted 1 June 2004

Abstract

Sabkha deposits in the geologic record are commonly used to interpret the environmental conditions of deposition. Implicit in this use is the assumption that the solute system is chemically closed, that is, the authigenic minerals represent the composition of the fluids in their environment of origin. Thermodynamic and mass-balance calculations based on measurements of water and solute flux of contemporary Abu Dhabi coastal sabkha system, however, demonstrate that the system is open for sodium and chloride, where nearly half of the input is lost, but closed for sulfur, where nearly 100% is retained. Sulfur and chloride isotopes were consistent with this observation. If these sabkha deposits were preserved in the geologic record, they would suggest a solute environment rich in sulfate and poor in chloride; yet the reverse is true. In most coastal-sabkha environments, capillary forces bring solutes and water to the surface, where the water evaporates and halite, carnallite, sylvite, and other soluble minerals are precipitated. Retrograde minerals, such as anhydrite, calcite, dolomite, and gypsum, however, precipitate and accumulate in the capillary zone beneath the surface of the coastal sabkha. Because they possess relatively low solubility and are below the surface, these retrograde minerals are protected from dissolution and physical erosion occurring from infrequent but intense rainfall events. Thus, they are more likely to be preserved in the geological record than highly soluble minerals formed on the surface.

Keywords: Abu Dhabi; Sabkha; Sedimentary Petrology; Hypersaline; Anhydrite

1. Introduction

In attempting to recreate the depositional environment of a sedimentary sequence, one typically evaluates the authigenic minerals preserved in the geologic record and infers the composition of fluid and temperature under which the minerals could have formed. Implicit in this process is the assumption of a closed system for solutes. To test the validity of this assumption, a modern coastal sabkha in the Emirate of Abu Dhabi was evaluated. Mass balance calculations demonstrated that the system is open for chloride, but

* Corresponding author. Tel.: +1 517 355 4629; fax: +1 517 353 8787.
E-mail address: wwwood@msu.edu (W.W. Wood).

0009-2541/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemgeo.2004.06.043

closed for sulfate, although the observed authigenic minerals suggest a solute source high in sulfate and low in chloride concentrations. Thus, the geologic record must be evaluated in light of system openness to determine the environment from which the minerals were derived.

Sanford and Wood (2001) discuss the hydrogeology, and Wood et al. (2002) address the origin of solutes of this sabkha system. This paper focuses on the origin and distribution of authigenic minerals in the coastal sabkha in an effort to evaluate quantitatively the solute-mass flux from which minerals are deposited in and on the coastal sabkha, and to compare that flux over time with the observed mass distribution of minerals. The difference between the calculated and observed mass gives a measure of the chemical openness of the system to different solutes, and thus gives some insight as to why the mineral assemblage in the Abu Dhabi coastal sabkha does not reflect the solute ratios of solutions from which the assemblage was derived.

2. Hydrogeological framework

Sabkhat (Arabic plural for "salt flats" or "salt surfaces") are ubiquitous features in many arid and semiarid areas of the world and constitute approximately 1% of the land surface. Typically, they are covered with halite and other soluble chloride and nitrate minerals (Smoot and Lowenstein, 1991; Rosen, 1994). The word sabkha has been used in geological literature for a mineralogy and texture that imply a three-dimensional system (Gary et al., 1972). "Sabkha" as used in this paper recognizes the original Arabic two-dimensional surface as part of a three-dimensional system, similar to the definition given by Kinsman (1969). The coastal sabkha in the Emirate of Abu Dhabi is exposed as a strip approximately 300 km long and 15 km wide (Fig. 1).

Polygons of halite approximately 1 m across and 1 to 2 cm thick, bordered by pressure ridges 2 to 3 cm high, cover much of the sabkha surface. The area is flat, with a topographic and groundwater gradient of approximately 1:5000 toward the Arabian Gulf, and with a depth between 0.5 and 1 m to groundwater. The Holocene rise of sea level starting at 18,000 years BP filled the Gulf to its present level by approximately 7000 years BP. As the sea level rose, sand from eolian Pleistocene dunes that existed in the area now occupied by the Gulf was incorporated into the Abu Dhabi Formation, upon which the coastal sabkha has developed (Evans, 1995). The eolian sand framework of the Abu Dhabi aquifer consists of uniform, fine-grained sand (0.16–0.22 mm) composed of 60% detrital carbonates and 35% quartz, with minor amounts of feldspar, anhydrite, and heavy minerals. Laboratory analysis of repacked sand yields a porosity of 0.38. Because of the uniformity and uncemented nature of the eolian sand, it is hypothesized that this value is also representative of the in situ porosity of the Abu Dhabi Formation.

The Abu Dhabi Formation, upon and within which the coastal sabkha is formed, is generally wedge-shaped, with zero thickness at the proximal edge and increasing to approximately 15 m near the coast (Butler, 1969; Fig. 2). These sands overlie Pleistocene and Miocene clastic rocks and older Tertiary evaporites in the coastal areas. The presence of paleochannels or erosional remnants of these rocks increases or decreases the thickness of the Abu Dhabi Formation. Superimposed on the Abu Dhabi Formation is the Evans Member, a thin (<2 m), wedge-shaped sand that starts midway between the proximal and distal edges of the sabkha and extends to the coast. The rate of progradation of the Evans Member into the Arabian Gulf is between 1 and 2 km every thousand years (Evans, 1995).

Authigenic anhydrite, calcite, dolomite, and gypsum are seldom present in significant quantities on the surface, and are largely confined to the capillary zone, which extends 0.5 to 1 m above the water table. In the areas investigated, most of the anhydrite consists of silt- or clay-size grains that give it a "toothpaste" consistency. Nodules of "chicken wire" anhydrite typically underlie this structureless anhydrite. Crystals of equidimensional gypsum up to 5 mm in length exist within the vertical range of the water-table fluctuations (Fig. 3). Minor amounts of authigenic calcite and dolomite are intermixed with the anhydrite. Visual inspection of exploration pits and auger cuttings suggests that anhydrite and gypsum have occluded approximately half of the porosity of the upper meter (Fig. 3).

Crusts of halite and other chloride and nitrate minerals form on the surface in different places, with

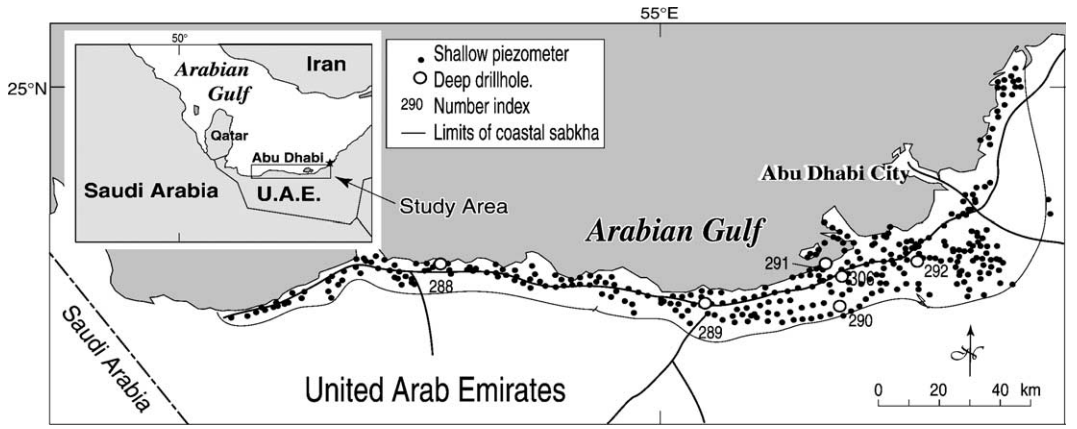

Fig. 1. Location of the coastal sabkha of the Emirates of Abu Dhabi, United Arab Emirates (U.A.E.). Points indicate chemical sampling locations within the aquifer underlying the sabkha (modified from Wood et al., 2002).

different thickness, and at different times throughout the year. Chloride minerals, however, are not readily apparent in the capillary zone or below the water table. Thin lines of dark-colored material (buried algal mats?) are observed only in the prograded Evans Member. X-ray diffraction identifications have shown that most of the evaporite minerals on the surface are halite, with trace amounts of carnallite, anhydrite, sylvite [KCl], and antarcticite (Daniel Webster, USGS, written communication, 2002). Results from chemical analyses of the soluble salts from the surface crusts are given in Table 1. Samples were collected from the surface by carefully lifting sections of the mineral crust and placing them in poly-sealed bags, assigning identifying numbers, and transporting them to the laboratory. Solute concentrations were determined after dissolution of the crust in distilled water by standard analytical methods (Wood et al., 2002). These analyses illustrate the large mass of chloride relative to sulfur on the sabkha surface, over a wide geographic area of several thousand square kilometers and are thus of a regional not local significance.

The average annual groundwater temperature at the water table in the sabkha is approximately 32 °C; the temperature on the surface can exceed 65 °C, thus giving a gradient of nearly 30 °C/m. The condition is reversed in the winter, however, with a negative temperature gradient of approximately 15 °C/m.

The capillary zone (rise of water above the water table) is critical to the development of the authigenic minerals in this environment. The zone results from two forces: mutual attraction between water molecules (hydrogen bonding), and molecular attraction between water and the different minerals that form the aquifer. Thus, for any given mineral, the smaller the interstitial pore size, the greater the vertical rise of water. The capillary rise (also called the "zone of tension saturation" or "wetting front") is the saturated zone above the water table in which the interstitial pore spaces are completely filled with water, but the water

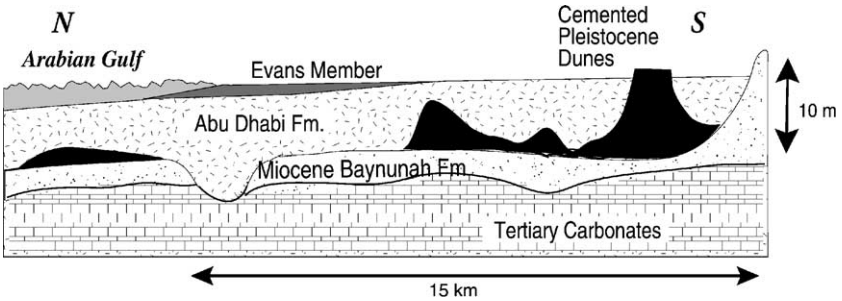

Fig. 2. Generalized geological cross section of the coastal sabkha of Abu Dhabi (modified from Wood et al., 2002).

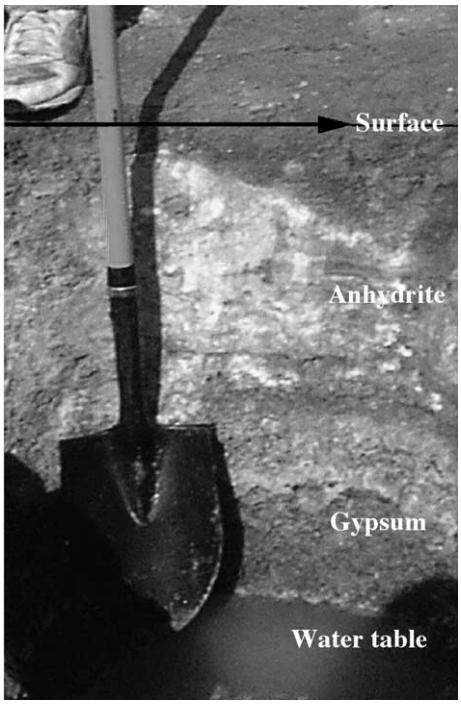

Fig. 3. A vertical profile of a representative test pit, showing the surface, capillary zone containing anhydrite and gypsum, and the water table in the coastal sabkha of Abu Dhabi.

is under less than atmospheric pressure. There can be no evaporation within this zone of tension saturation because water completely fills the pore spaces. Above the zone of tension saturation is a zone in which the water film and a gas phase exist in the interstitial pore space. The relative humidity of this gas phase is, however, equal to the thermodynamic activity of water, and no evaporation occurs. Evaporation occurs at, or a few centimeters below, the surface where the relative humidity of the gas phase is less than the thermodynamic activity of the water. Thus, minerals formed in the lower two environments are not evaporites, but are thermalites. A thermalite is herein defined as a mineral formed by changes in temperature independent of other processes that alter the thermodynamic properties of the solution.

The average residence time for water in the capillary zone of 1 m thickness is calculated using Eq. (1):

$$R_w = VS\theta/E, \quad (1)$$

where R_w is the residence time for water (T), V is the volume of the capillary zone (L^3), θ is the total porosity (dimensionless), S is the water saturation porosity (dimensionless), and E is the evaporation flux rate ($L^3\ T^{-1}$), where L is length, and T is time. With observed values of the parameters (V=1 m^3, θ=0.38, S=0.5, and E=0.065 $m^3\ year^{-1}$), the residence time for water in the capillary zone is between 1 and 2 years.

The conceptual model proposed herein for mineral deposition on most coastal sabkhat suggests that water and solutes are transported upward by capillary force from the shallow water table in response to water evaporating at the surface. The water is removed, leaving salts that form halite [NaCl], carnallite [$KMgCl_3 \cdot 6H_2O$], antarcticite [$CaCl_2 \cdot 6H_2O$], and other soluble minerals. Minerals exhibiting retrograde solubility, however, such as anhydrite [$CaSO_4$], calcite [$CaCO_3$], dolomite [$CaMg(CO_3)_2$], and gypsum [$CaSO_4 \cdot 2H_2O$], are precipitated below the surface as

Table 1
Chemical analyses (μg g^{-1}) of soluble surface crusts from the Abu Dhabi sabkha

Site name	UTM easting	UTM northing	UTM zone	Ca	Mg	Na	K	Sr	SiO_2	Cl	NO_3	SO_4
C	609434	2647570	39	2792	2204	80,000	1469	73	13	144,521	212	6527
A	628728	2650813	39	6163	3698	100,000	2157	154	26	195,520	800	6703
E	654839	2665053	39	2130	913	91,000	1126	33	10	157,286	435	5915
G	709433	2266465	39	1679	1068	130,370	1373	37	78	386,032	516	9734
B	733623	2661480	39	3586	14,943	101,000	897	105	18	197,252	215	9661
F	734060	2653098	39	2541	291	15,000	598	36	16	25,527	316	8343
TR-099	777530	2655420	39	5895	1474	106,000	1832	95	17	228,300	543	10,506
GWP-289	777587	2655712	39	4941	898	112,000	1422	85	19	248,967	467	9278
D	794944	2661406	39	6870	1754	93,000	1169	105	21	169,117	493	10,176
Abu -110	205454	2670505	40	5487	968	136,330	1614	97	24	419,991	233	9915
RP-6	205638	2670541	40	1305	657	13,800	600	32	5	40,277	52	2651
RP-1	207424	2668784	40	3455	2356	12,050	1286	53	17	38,643	147	5531
RP-5	210950	2655364	40	626	746	11,340	373	69	33	26,101	213	1950

a result of increasing temperature as the solutes move from the groundwater through the capillary zone toward the surface during the summer months.

3. Water and solute transport

Wood et al. (2002) have shown that most of the solutes in the Abu Dhabi aquifer are derived from the underlying Tertiary brines, whereas most of the water is a result of direct recharge of precipitation on the sabkha surface (Sanford and Wood, 2001). Consider a rectilinear volume of Abu Dhabi aquifer perpendicular to the coast and defined as 1 m wide, 10 m deep, and 10 km long. Hydrological analysis suggests that each year within this rectilinear volume, less than 1 m^3 of water enters and exits by lateral groundwater flow, 45 m^3 of water enter by upward vertical leakage, and 640 m^3 of water enter by recharge from rainfall. Approximately the same amount is lost each year by evaporation (Sanford and Wood, 2001). In contrast, 100 kg of solute enter through lateral groundwater flow, 200 kg are discharged to the Gulf through lateral groundwater flow, rainwater introduces 15 kg, and upward vertical leakage introduces 3700 kg (Wood et al., 2002). Water has a residence time of approximately 50 years, whereas solutes have a residence time of approximately 26,000 years in the sabkha.

Because of the low values of hydraulic conductivity and gradient, only a small mass of total solutes that have entered the Abu Dhabi Formation have discharged to the Gulf. Thus, solute concentrations increase over time as a result of the addition of new solutes from the underlying Tertiary formations, lateral groundwater flow, and the recycling of soluble salts returned by surface recharge. Hydraulic potential, density, and Rayleigh numbers calculated from 12 pairs of piezometers at the top and bottom of the aquifer suggest vertical mixing (Sanford and Wood, 2001). The observation that tritium exists throughout the vertical profile (McKenzie et al., 1980) is consistent with this vertical circulation and the short residence time of water in the sabkha.

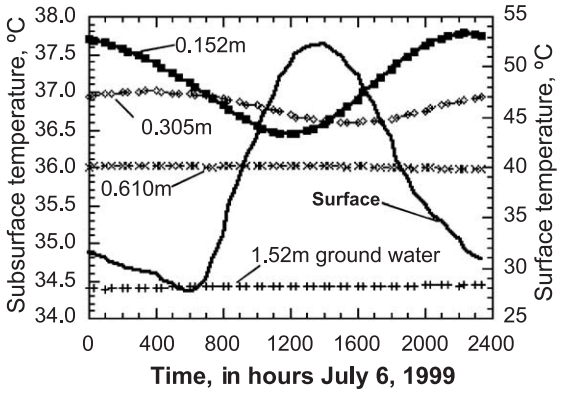

Fig. 4. One day temperature record of the surface, at various depths in the capillary zone, and of groundwater in the coastal sabkha of the Emirates of Abu Dhabi.

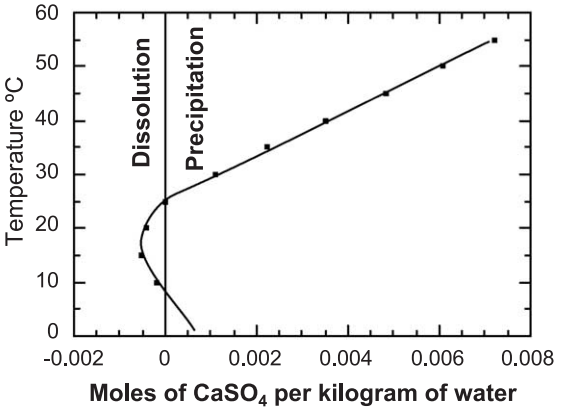

Fig. 5. Moles of $CaSO_4$ precipitated per kilogram of water as a function of temperatures for a representative solute sample from the sabkha of the Emirates of Abu Dhabi.

Water and solutes in the coastal sabkha water are close to or at thermodynamic equilibrium with respect to anhydrite, calcite, gypsum, and halite in most of the 192 water samples evaluated. It is proposed that precipitation of retrograde minerals occurs in the summer as the water warms during its transport to the surface. To evaluate the thermal gradient, the temperature of the surface, and the temperature at three depths in the capillary zone and one depth in shallow ground were collected at 15-min intervals for 9 months. A representative summer day (July 6, 1999) illustrates a positive gradient of approximately 25 °C/m (Fig. 4).

Reverse thermal gradient in the winter permits dissolution of some of the previously precipitated retrograde minerals. Because the negative thermal gradient is less in the winter than in the summer with nearly the same water flux, the water does not have the capacity to dissolve all of the mineral mass that was precipitated in the preceding summer. Thus, there is a

net accumulation of these retrograde minerals in the capillary zone. This analysis assumes that the equal winter and summer water flux found by Sanford and Wood (2001) is representative of the long-term environment. The difference in mass precipitated and dissolved as a function of temperature is illustrated for anhydrite (Fig. 5) and defines the relatively small temperature range during which dissolution in winter can occur.

4. Solute mass balance

Comparison between the mass introduced by the vertical solute fluxes and the observed mineral accumulation corroborates the proposed capillary transport model. Consider a saturated vertical column $1\times1\times9$ m, with a porosity of 0.38. One pore volume of this column occupies 3.4 m^3, or 3,420,000 cm^3. The underlying Tertiary brines have an average sulfate concentration of 4.7 g l^{-1} (Table 2). Solute samples in Table 2 were collected and analyzed by methods described in Wood et al. (2002). Table 2 provides samples from a wide geographic range of several hundred kilometers illustrating that data are not a local phenomena. It is known from the hydrology that the input solutes from the underlying brine would have been concentrated approximately seven times since the aquifer was formed (Sanford and Wood, 2001). Thus, if the water flux and sulfate concentration have remained constant over 7000 years, approximately 33 g l^{-1} of sulfate would have been delivered to the control volume. The observed dissolved-sulfate concentration in the coastal sabkha aquifer of 4 g l^{-1} (Table 2) suggests a loss of approximately 29 g l^{-1} over time. This mass loss per liter is multiplied by the number of liters in the control volume, which results in a total loss from solution of 98,200 g in 7000 years. Assuming that all of this loss is due to the precipitation of anhydrite with a molecular weight of 136, then a mass of 139,000 g would have been precipitated in our control volume since the Abu Dhabi aquifer was formed. As anhydrite has a density of 2.94 g cm^{-3}, 47,300 cm^3 of pore space in our control volume is occluded by this mineral. A comparison of this volume to total pore space can be made using the following formula

$$\theta_f = V_{min}/V_{tot}, \quad (2)$$

where θ_f is the fraction of total porosity occupied by anhydrite, V_{min} is the volume of minerals precipitated, and V_{tot} is the total pore volume. If it is assumed that most of this loss occurs in a capillary zone that extends to 0.5 m above the water table, then the fraction of total porosity occupied by anhydrite is approximately 25%, which is consistent with the observed mass of anhydrite.

The thermodynamic approach provides another independent estimate of the mass precipitated. In this approach, the geochemical code PHRQPITZ (Plummer et al., 1988) is used with a representative solute analysis of the water from the sabkha to calculate the amount of anhydrite precipitated at various temperatures. The flux rate of water vapor is between 0.15 and 0.2 mm/day, or approximately 65 mm annually. This rate does not vary significantly throughout the seasons of the year (Sanford and Wood, 2001). For a 1-m^2 surface area, this flux translates into 65 l a^{-1}, or 75 kg a^{-1}, and represents the water flux that can be used in the calculations. Assuming that the average annual temperature of the capillary zone is 40 °C, then it is possible to calculate a net anhydrite precipitation of approximately 0.26 mol a^{-1} m^3, or 35 a^{-1} m^3 (Fig. 5). Using a density of 2.94 g cm^{-3}, approximately 12 cm^3 a^{-1} m^3 of pore space is filled with anhydrite each year. Because this system has been operating for approximately 7000 years, a total of 84,500 cm^3 of pore space would now be filled with anhydrite. Application of Eq. (2) suggests that approximately 45% of the available pore space in the capillary zone would be occupied by anhydrite. It is assumed that all of the sulfate is removed in the capillary zone (100% efficient), which is not the case because minor amounts of sulfate occur in the surface salt crusts (Table 1). Thus, the 45% reduction in porosity is a maximum value and is consistent with the value of 25% calculated by the mass-balance method, considering the uncertainties of each method.

Sulfur-isotope data, expressed as $\delta^{34}SSO_4$ (Table 3), are consistent with a closed system for S. That is, loss of sulfate from the system would distort the isotopic ratio of the remaining solutes and minerals. The $\delta^{34}SO_4$ is defined as:

$$\delta^{34}SO_{4\,CDT} = \left(R_{sample} - R_{CDT}\right)/\left(R_{CDT}\right) \times 1000, \quad (3)$$

Table 2
Chemical and isotopic analyses of selected samples

Field numbers	UTM east	UTM north	UTM zone	Date sampled	Ca (mg l^{-1})	Mg (mg l^{-1})	Na (mg l^{-1})	K (mg l^{-1})	Sr (mg l^{-1})	SiO_2 (mg l^{-1})	Alk HCO_3	Cl (mg l^{-1})	SO_4 (mg l^{-1})	NO_3 (mg l^{-1})	Br (mg l^{-1})	B (μg l^{-1})	Ba (μg l^{-1})	Density at 20 °C	δ^2H (‰)	$\delta^{18}O$ (‰)	$\delta^{37}Cl$ (‰)	pH	Dissolved solids
Coastal sabkha aquifer																							
ABU-007	251309	2669821	40	29-Dec-97	12,900	13,400	83,000	5550	220	51	13	200,000	750	2000	130	3300	760	1.2127	31.9	8.83	0.07	6.1	318,000
ABU-012	250900	2688981	40	30-Dec-97	8250	14,400	81,500	4800	200	41	16	190,500	900	1700	35	1200	480	1.2033	25.3	6.05	0.38	6.5	302,300
ABU-017	235103	2678219	40	30-Dec-97	40,000	31,000	40,300	13,600	900	101	20	240,000	200	8400	50	880	2300	1.2622	27.3	6.76	0.36	5.6	374,370
ABU-024	238042	2675163	40	4-Jan-98	15,800	17,900	71,500	7100	225	56	12	197,000	650	4400	15	1300	480	1.2120	28.9	7.12	−0.20	6.0	314,700
MAT-001	578676	2649822	39	9-Dec-97	2900	5800	88,000	2650	90	26	8.5	166,000	2500	650	80	7000	640	1.1828			−0.06	6.5	268,700
MAT-026	619369	2647143	39	16-Dec-97	5600	7700	92,000	4200	140	32	32	177,000	1700	140	85	2800	340	1.1862			0.31	6.5	288,600
MAT-038	628002	2646412	39	17-Dec-97	26,900	20,500	64,500	6250	700	60	21	204,000	250	14,700	20	2400	2100	1.2245			−0.04	6.1	337,900
GWP 287c	600314	2647259	39	Feb-98	2000	1775	21,000	775	35	21	79	36,500	4300	315		8350	25	1.0452	17.8	6.12	0.09		67,300
GWP 288b	687881	2666667	39	Feb-98	3500	3750	63,000	1450	65	29	45	105,000	2800	1100		7500	90	1.1312	26.4	7.83	−0.19	7.6	186,800
GWP 288b																					−0.30		
GWP 291b	205540	2670460	40	Feb-98	4250	4700	81,500	2650	75	33	36	157,000	2150	33		4500	80	1.1693	27.3	6.27	0.43	7.4	256,000
Average of 192 analyses of sabkha					11,250	10,000	82,120	4240	262	52	56	176,350	3920	3550	80			1.1896				6.6	291,930
Tertiary brine inout																							
GWP 288a	687801	2666649	39	Feb-98	1450	950	10,500	300	25	36	55	19,700	4050	33	11	23,000	20	1.0258	−6.2	2.37	0.12	8.0	37,110
GWP 289	777650	2655600	39	Feb-98	1150	675	5600	120	23	15	49	10,300	4000	8	5	4250	10	1.0146	0.7	2.92	−0.10	7.8	21,900
GWP 290	211100	2655224	40	Feb-98	1500	950	15,500	450	27	20	50	25,000	6750	22	15	9250	10	1.0369	5.9	4.09	0.16	7.4	50,280
GWP 291a	205540	2670460	40	Feb-98	2200	1350	31,500	950	40	18	39	55,100	4650	35	20	10,500	5	1.0686	5.0	4.64	0.44	7.8	95,900
GWP 291a																					0.35		
GWP-292	236945	2671480	40	Feb-98	3600	2400	48,000	1500	62	23	34	87,300	3300	33	6	14,700	15	1.0971	7.5	5.19	−0.01	7.4	146,300

Table 3
Sulfur-isotope values of solutes

Site number	UTM east	UTM north	UTM zone	Date sampled	SO_4 (mg l^{-1})	$\delta^{34}S$ (‰)	Depth (m), BLS
Coastal sabkha solutes							
ABU 024	238042	2675163	40	03-Jan-98	650	18.9	2 to 3
ABU 039	214202	2666488	40	05-Jan-98	850	16.9	2 to 3
ABU 134	253864	2663357	40	23-Mar-98	950	14.4	2 to 3
ABU 195-S	211348	2664564	40	24-Mar-98	950	14.0	2 to 3
GWP 287-C	600314	2647259	39	Feb-98	4300	18.4	5 to 6
GWP 288-B	687811	2666667	39	Feb-98	2800	16.9	5 to 6
MAT 015	598286	2631893	39	08-Dec-97	750	15.5	2 to 3
MAT 041	619337	2636708	39	21-Dec-97	600	13.0	2 to 3
MAT 049	610965	2623284	39	21-Dec-97	100	14.7	2 to 3
RUW 010	638992	2656711	39	13-Dec-97	1000	16.1	2 to 3
RUW 033	688683	2667926	39	02-Mar-98	1200	14.1	2 to 3
RUW 048	712600	2667300	39	11-Mar-98	4000	13.9	2 to 3
TAR 004	796039	2661669	39	15-Feb-98	1150	18.2	2 to 3
Tertiary brine input							*-cm-*
GWP-288A	687801	2666649	39	Feb-98	4050	19.8	89
GWP-289	777587	2655712	39	Feb-98	4000	19.8	119
GWP-290A	210989	2655365	40	Feb-98	6750	17.7	88
GWP-291A	205481	2670574	40	Feb-98	4650	18.4	142
GWP-292	236909	2671579	40	Feb-98	3300	17.8	119
Sabkha anhydrite							
Site 1	207444	2668779	39	12-May-97	–	20.5	0.010–.038
Site 1	207444	2668779	39	12-May-97	–	20.1	0.013–.018
Site 1	207444	2668779	39	12-May-97	–	19.8	0.027
Site 2	203552	2673333	39	12-May-97	–	20.4	0.0–.015
Site 2	203552	2673333	39	12-May-97	–	21.3	0.089–.109
Site 2	203552	2673333	39	12-May-97	–	21.2	0.134–.147
Site 4	209275	2660028	39	13-May-97	–	17.2	0.0–.015
Site 4	209275	2660028	39	13-May-97	–	17.2	0.030–.046
Site 4	209275	2660028	39	13-May-97	–	17.2	0.058–.073

where R_{sample} is $^{34}SO_4/^{32}SO_4$ of the sample, and R_{CDT} is $^{34}SO_4/^{32}SO_4$ of the standard Canyon Diablo troilite (CDT). Samples in Table 3 were collected and analyzed by methods described in Wood et al. (2002) and illustrate the similarity of results over a large geographic area.

It is known from isotopic fractionation experiments that gypsum precipitated from a solution will be about 1.65‰ (per mil) heavier than input, and that the sulfate remaining in solution will be about 1.65‰ lighter than the input (Thode and Monster, 1965). Analyses in Table 3 indicate that the average of five samples of Tertiary brine is 18.7‰. Thus, anhydrite or gypsum that precipitates in the unsaturated zone should average approximately 20.35‰ and the sulfate remaining in solution in the Abu Dhabi aquifer should average 17.0‰. It is seen in Table 3 that the average of 9 samples of these minerals from the unsaturated zone is 20.0‰, and the average of 13 samples of sulfate from the Abu Dhabi aquifer is 15.8‰. The observed values are close to those predicted by fractionation from the Tertiary brines and are consistent with the model that little sulfate has been lost from the system. The isotopic values from the sediments differ from those reported by Butler et al. (1973) because the samples were collected outside the supratidal zone examined by Butler et al. (1973), and thus they do not have the seawater isotopic signature.

A mass-balance calculation for Cl and Na similar to that above suggests that there should be a layer of halite approximately 30 cm thick on the surface. Commonly, there is less than 1 cm and none in the capillary zone or below the water table. Thus, the system has lost a significant amount of Na and Cl. Fig. 6, plotted from analyses of 192 samples of water collected from representative areas of the coastal sabkha (Fig. 1), shows the evolution and loss of Na

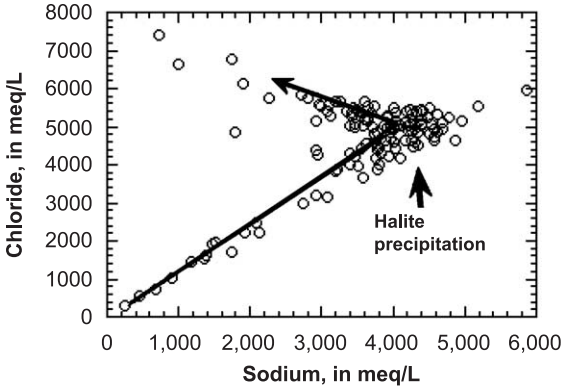

Fig. 6. Milliequivalents per liter (meq l^{-1}) of Na as a function of meq l^{-1} of Cl illustrates the evolution of Na concentration in the sabkha of the Emirates of Abu Dhabi.

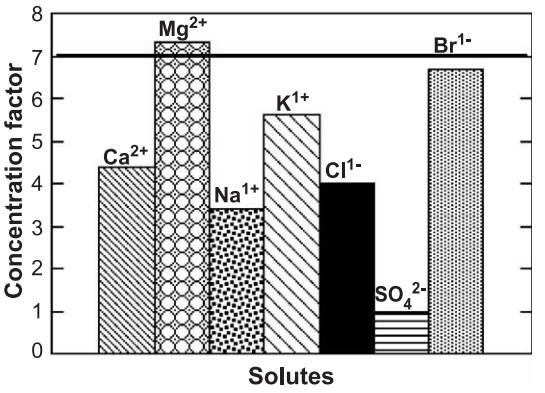

Fig. 7. Concentration factor (ratio of existing concentration in the sabkha aquifer to input concentration of Tertiary brines) of the coastal sabkha aquifer of the Emirates of Abu Dhabi. Line at a concentration factor of 7 is that calculated from physical hydrological information (modified from Wood et al., 2002).

(halite) from solution. Calculating the amount of halite loss from the concentration ratio of a given solute provides a means of estimating loss (Fig. 7), as shown in the following equation:

$$\mathrm{CR} = C_{\mathrm{obs}}/C_{\mathrm{in}}, \tag{4}$$

where CR is the concentration ratio, C_{obs} is the observed solute concentration, and C_{in} is the solute concentration of input solute.

It is known that the concentration ratio in the Abu Dhabi sabkha aquifer is approximately 7 for essentially conservative solutes, such as Br and Mg (Fig. 7; Table 2). Conversely, the concentration ratio for Na is 3.5 (Fig. 7). This difference in concentration ratio is most easily explained by assuming that approximately one-half of the Na has been removed from solution by precipitation as halite. Because there is little halite in the system, it is concluded that the system is chemically open with respect to Na and Cl.

Isotopes of Cl can also provide insight into the evolution of Cl in this system. The δ^{37}Cl isotope is defined as follows:

$$\delta^{37}\mathrm{Cl}_{\mathrm{SMOC}} = \left(R_{\mathrm{sample}} - R_{\mathrm{SMOC}}\right)/\left(R_{\mathrm{SMOC}}\right) \times 1000, \tag{5}$$

where R_{sample} is $^{37}\mathrm{Cl}/^{35}\mathrm{Cl}$ of the sample, and R_{SMOC} is $^{37}\mathrm{Cl}/^{35}\mathrm{Cl}$ of the standard SMOC (Standard Mean Ocean Chlorine). The value of δ^{37}Cl was calibrated using seawater (Atlantic Ocean), which has been matched to the worldwide seawater standards of Kaufman et al. (1984). Filtered, unacidified water samples were used for δ^{37}Cl analyses. Chloride in solution was removed as silver chloride using silver nitrate and converted to methyl chloride, according to the method described by Long et al. (1993). Pretreatment to remove sulfate was not observed to affect the final result. Methyl chloride samples were analyzed using a VG SIRA 9 mass spectrometer. The triple collector geometry allows for the measurement of individual SO and S2 mass peaks. Analytical precision of the technique in use for this study was ±0.15‰. Results of these analyses are presented in Table 2.

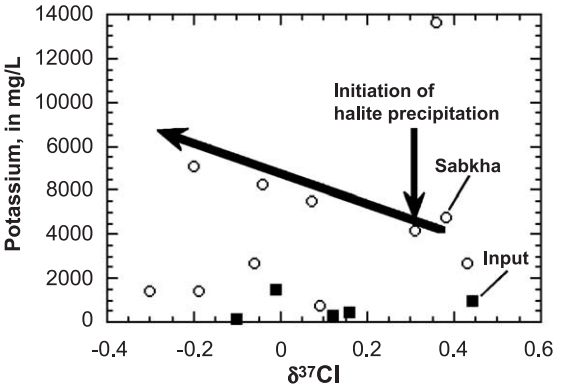

Fig. 8. Chlorine isotopes versus concentration of K of both sabkha (○) and input Tertiary brine (■) from Table 2 illustrate the decrease in isotopic value with increasing concentration of K once halite precipitation has commenced.

The dissolved Cl becomes isotopically lighter with increasing concentration of K (Fig. 8), consistent with the precipitation of halite and preferential removal of ^{37}Cl relative to ^{35}Cl. Concentrations of K that are <3000 mg l^{-1} and that have $\delta^{37}Cl$ ranging from −0.2 to 4.0 represent input values that are concentrated by evaporation, but no mechanism is operating to cause isotopic fractionation. It is only after the start of precipitation of halite that $\delta^{37}Cl$ becomes more negative with increasing concentration of K (Long et al., 1993; Fig. 8). Although the value of $\delta^{37}Cl$ by itself does not assist with defining an open system, the observation that it changes has important ramifications for interpreting the isotopic record of Cl in sabkha sediments.

5. Mechanisms of mass loss from the system

The mechanism or combination of mechanisms by which halite is lost from the surface is not known with certainty. Halite may be removed from the surface by eolian processes or by dissolution and transport to the Arabian Gulf. Because the halite on the sabkha is more "ice-like" than the loose, fine powder common with Na sulfates or Na carbonates, it is not as mobile in an eolian setting. Two sets of eolian samplers 100 km apart did detect some mass transport in the 2 years of the study; however, data collection was poor, and the results are not definitive. The concentration ratios for Mg and K ions are different from those of Na and Cl (Fig. 7), suggesting selective removal rather than the loss of all surface salts (Table 1) that would be expected to occur by eolian erosion.

Solute transport into the adjacent Arabian Gulf could occur either by flooding of Gulf water or by rainfall runoff. Because the halite is missing over the entire area, not just seaward of the high stand of the supratidal zone, located approximately 3 km inland, encroachment by Gulf floodwater does not appear to be a viable mechanism for surface-salt removal. The annual rainfall along the coast averages 60 mm; however, it is known that approximately 100 mm of rain occurred once in a 24-h period in the 35 years for which records exist (Bottomley, 1996). It is concluded that the most likely scenario for removing the soluble surface crust is the intense but infrequent rainfall events that dissolve and transport salts to the Arabian Gulf.

A check on the reasonableness of this explanation for halite dissolution by intense rainfall is obtained by calculating the amount of halite that could be dissolved with a 100-mm rainfall. Consider a surface area 1 m^2. It is known that Cl concentration in equilibrium with halite in this system, from Fig. 6, is approximately 142,000 mg l^{-1}. One hundred millimeters of rain is equivalent to 100 l on the 1 m^2 control surface area. Thus, the dissolution potential is 14,200 g of Cl, or 21,900 g of halite. Halite has a density of 2.16 g cm^{-3}, so approximately 10,100 cm^3 of halite could be removed, or a thickness of approximately 1 cm on the 1-m^2 control area. It is known from the analysis above that approximately 30 cm of halite are missing. Thus, it would take only one 100 mm/day rainfall to occur once in every 230 years of the 7000 years the system has existed, to remove the halite. Only 35 years of rainfall data exist, but it seems probable that the 100 mm/day rainfall occurs more frequently than once in 230 years. Thus, the proposed rainfall–dissolution-transportation mechanism is not constrained by dissolution potential.

The observation that the concentration ratios of K, Mg, and Br are closer to the input values is also consistent with the rainfall–dissolution model. If the salts were removed by eolian activity, all salts would be removed in equal ratios, which is not observed. The following model is thus proposed: the more soluble minerals, such as carnallite, sylvite, and antarcticite, would be the first to dissolve, and thus selectively recharged relative to NaCl in any recharge event. The presence of only a small volume of storage in the capillary zone limits the amount of water that can be recharged in any one event because the first water in a recharge event fills the available space, and the rest is rejected. With continued rain, the pools in the polygons coalesce and flow down-gradient toward the Gulf, removing the less soluble halite. The net result is that there is a lack of mass balance among the Na, K, Mg, and Ca present in the sabkha relative to the input solutes.

6. Summary and conclusions

The conceptual model developed above suggests that water and solutes are transported upward by capillary force from the shallow water table in response to evaporation of water at the surface. The water is

removed, thereby precipitating halite, carnallite, antarcticite, and other soluble minerals. Minerals exhibiting retrograde solubility, however, such as anhydrite, calcite, dolomite, and gypsum, are precipitated below the surface as a result of increasing temperature as the solutes move from the groundwater through the capillary zone toward the surface during the summer months. The difference in thermal gradient between the winter and summer months is consistent with the net accumulation of these minerals over time in the capillary zone. Because these minerals are rather insoluble relative to halite and other chloride and nitrate minerals, and are precipitated below the surface, they are less likely to be dissolved and transported to the Gulf by rainfall, and thus they are preserved selectively relative to the soluble salts on the surface.

The observations above are important in evaluating the solute environment responsible for the chemical sediments preserved in the geological record. That is, the system is chemically open for Cl and closed for S, and the mass of a given mineral preserved depends upon factors other than the original solute composition. Mineral development in the coastal sabkha is conceptually similar to the leaky-basin model (open system) used to understand mineral development in evaporating basins (Wood and Sanford, 1990; Sanford and Wood, 1991) and contrasts with the closed system approach of Hardie and Eugster (1970). The preferential loss of halite, and possibly other soluble minerals, from this system is important in understanding the evolution of solute chemistry and mineral development in coastal sabkhat and has implications for evaluating coastal-sabkha facies and environments in the geological record. It is important to note that the system can be closed for one element and open for another, and likewise that water may be derived from one source and solutes from another. Because of these factors, care must be used in interpreting the solute environment of a coastal sabkhat solely on the basis of the mineralogical record.

Acknowledgments

We thank Mohamed B. Al-Qubaisi, Abu Dhabi National Oil Company, UAE, for his interest and support, and John Czarnecki, U. S. Geological Survey (USGS), for installing the temperature probes and supervising the collection of the temperature data. We also thank Thomas Kraemer, USGS, and Duncan Sibley, Michigan State University, for their efforts in the early review process. Sibley also provided X-ray analyses of some of the minerals. Jeffery Hanor, Michael Rosen, and Robert Seal provided insightful and helpful reviews. Publication is approved by the Director of the USGS and the Abu Dhabi National Oil Company. The investigation was fully funded by Abu Dhabi National Oil Company. **[PD]**

References

Bottomley, N., 1996. Recent climate in Abu Dhabi. In: Osborne, P.E. (Ed.), Desert Ecology of Abu Dhabi. Pisces Publications, Newbury, UK.

Butler, G.P., 1969. Modern evaporite deposition and geochemistry of coexisting brines, the sabkha, Trucial Coast, Arabian Gulf. J. Sediment. Petrol. 39, 70–81.

Butler, G.P., Krouse, R.H., Mitchell, R., 1973. Sulphur-isotope geochemistry of an arid, supratidal evaporite environment, Trucial Coast. In: Purser, B.H. (Ed.), The Persian Gulf. Springer-Verlag, Berlin, pp. 453–462.

Evans, G., 1995. The Arabian Gulf—a modern carbonate–evaporite factory; a review. Cuadernos de Geologia Iberica, vol. 19. Servicio de Publicaciones, Universidad Complutense, Madrid, pp. 61–95.

Gary, M., McAfee, R., Wolf, C.L. (Eds.), Glossary of Geology. American Geological Institute, Washington, DC.

Hardie, L.A., Eugster, H.P., 1970. The evolution of closed-basin brines. Mineral. Soc. Am. Spec. Publ. 3, 273–290.

Kaufman, R., Long, A., Bentley, H., Davis, S., 1984. Natural chlorine isotope variation. Nature 309, 338–340.

Kinsman, D.J.J., 1969. Modes of formation, sedimentary associations, and diagnostic features of shallow-water and supratidal evaporites. Am. Assoc. Pet. Geol. Bull. 53, 830–840.

Long, A., Eastoe, C., Kaufman, R.S., Martin, J.G., Wirt, L., Finley, J.B., 1993. High-precision measurements of chlorine stable isotope ratios. Geochim. Cosmochim. Acta 57, 2907–2912.

McKenzie, J.A., Hsü, K.J., Schneider, J.F., 1980. Movement of subsurface waters under the sabkha, Abu Dhabi, UAE, and its relation to evaporative dolomite genesis. SEPM Spec. Publ. 28, 11–30.

Plummer, L.N., Parkhurst, D.L., Fleming, G.W., Dunkle, S.A., 1988. A computer program incorporating Pitzer's equations for calculation of geochemical reactions in brines. U.S. Geol. Surv. Water-Resources Invest. Rep. 88–4153.

Rosen, M.R., 1994. The importance of groundwater in playas: a review of playa classifications and the sedimentology and hydrology of playas. Spec. Pap.-Geol. Soc. Am. 289, 1–18.

Sanford, W.E., Wood, W.W., 1991. Brine evolution and mineral deposition in hydrologically open evaporite basins. Am. J. Sci. 291, 687–710.

Sanford, W.E., Wood, W.W., 2001. Hydrology of the coastal sabkhas of Abu Dhabi, United Arab Emirates. Hydrogeol. J. 4, 358–366.

Smoot, J.P., Lowenstein, T.K., 1991. Depositional environments of non-marine evaporites. In: Melvin, J.L. (Ed.), Evaporites—Petroleum and Mineral Resources, Developments in Sedimentology, vol. 50. Elsevier, Amsterdam, pp. 189–347.

Thode, H.G., Monster, J., 1965. Sulfur-isotope geochemistry of petroleum, evaporites, and ancient seas. Am. Assoc. Pet. Geol. Bull. 4, 367–377.

Wood, W.W., Sanford, W.E., 1990. Groundwater control of evaporite deposition. Econ. Geol. 85, 1226–1235.

Wood, W.W., Sanford, W.E., Al Habshi, A.R.S., 2002. The source of solutes to the coastal-sabkha aquifer of Abu Dhabi. Geol. Soc. Amer. Bull. 114, 259–268.